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HIGHLY PURE HAFNIUM MATERIAL, TARGET AND THIN FILM COMPRISING THE SAME AND METHOD FOR PRODUCING HIGHLY PURE HAFNIUM

TECHNICAL FIELD

The present invention relates to a high purity hafnium material with a reduced zirconium content contained in the hafnium, a target and thin film formed from this material, and a manufacturing method of high purity hafnium.

BACKGROUND ART

Conventionally, there are numerous documents relating to the manufacture of hafnium, and, since hafnium and zirconium are very similar in terms of atomic structure and chemical property, the inclusion of zirconium or the inclusion of zirconium in hafnium was never really acknowledged as a problem as exemplified below.

Hafnium and zirconium are superior in heat resistance and corrosion resistance, and are characterized in that they have a strong affinity with oxygen and nitrogen. And, since the oxides or nitrides thereof have superior stability in high temperatures, they are utilized as ceramics in the atomic power generation or as fire-resistant materials in the manufacture of steel or castings. Further, recently, these are also being used as electronic materials or optical materials.

The manufacturing method of metal hafnium or metal zirconium is proposed as the same manufacturing method. As such example, there is a method of reacting a fluorine-containing zirconium or hafnium compound with metal aluminum or magnesium in inert gas, reducing gas or vacuum at a temperature of 400°C or higher (e.g., refer to Japanese Patent Laid-Open Publication No. S60-17027); a manufacturing method of reducing zirconium chloride, hafnium chloride or titanium chloride to obtain the respective metals thereof characterized in the sealing metal (e.g., refer to Japanese Patent Laid-Open Publication No. S61-279641); a manufacturing method of hafnium or zirconium characterized in the reaction container structure upon reducing zirconium tetrachloride or hafnium tetrachloride

with magnesium and the manufacturing technique thereof (e.g., refer to Japanese Patent Laid-Open Publication No. S62-103328); a method of manufacturing chloric-, bromic- or iodic- zirconium, hafnium, tantalum, vanadium or niobium compound vapor by introducing these into a crucible (e.g., refer to PC(WO)1991-501630); a method of refining zirconium or hafnium chloride or an acid chloride aqueous solution with strongly basic anion exchange resin (e.g., refer to Japanese Patent Laid-Open Publication No. H10-204554); and a method of collecting zirconium via solvent extraction (e.g., refer to Japanese Patent Laid-Open Publication No. S60-255621).

As described in the foregoing documents, although there are numerous refining methods and extraction methods of zirconium and hafnium, the inclusion of zirconium or the inclusion of zirconium in hafnium was never really acknowledged as a problem.

Nevertheless, in recent years, deposition on electronic components using hafnium silicide is being demanded. In such a case, even zirconium is an impurity, and there is a possibility that the required characteristics of the hafnium raw material may become unstable. Therefore, there is demand for a high purity hafnium material with reduced zirconium, and a target and thin film formed from such a material.

However, since there was no notion of separating hafnium from zirconium as described above, the actual condition is that there is no efficient and stable manufacturing technology for obtaining the foregoing high purity hafnium material with reduced zirconium, and a target and thin film formed from such a material.

DISCLOSURE OF THE INVENTION

Thus, the present invention relates to a high purity hafnium material with a reduced zirconium content contained in the hafnium, a target and thin film formed from this material, and a manufacturing method of high purity hafnium, and an object thereof is to provide efficient and stable manufacturing technology, a high purity hafnium material obtained according to such manufacturing technology, and a target and thin film formed from such material.

In order to achieve the foregoing object, as a result of intense study, the present inventors discovered that high purity hafnium can be manufactured by

separating zirconium via solvent extraction, and performing electron beam melting thereto.

Based on the foregoing discovery, the present invention provides:

1. A high purity hafnium material, and a target and thin film formed from this material, wherein the zirconium content is 1 to 1000wtppm, and the purity thereof is 4N to 6N excluding gas components such as carbon, oxygen and nitrogen;

2. The high purity hafnium material, and the target and thin film formed from this material according to paragraph 1 above, wherein oxygen is 500wtppm or less, nitrogen and carbon are respectively 100wtppm or less, iron, chromium and nickel are respectively 10wtppm or less, and the purity thereof is 4N to 6N excluding gas components such as carbon, oxygen and nitrogen;

3. A manufacturing method of high purity hafnium including the steps of making aqueous solution of chloride of hafnium, thereafter removing zirconium therefrom via solvent extraction, performing neutralization treatment to obtain hafnium oxide, further performing chlorination to obtain hafnium chloride, and reducing this to obtain a hafnium sponge;

4. The manufacturing method of high purity hafnium according to paragraph 3 above, wherein the moisture content in the hafnium chloride before reduction and in the atmosphere is 0.1wt% or less, and the nitrogen content therein is 0.1wt% or less;

5. The manufacturing method of high purity hafnium according to paragraph 3 or paragraph 4 above, wherein the reduction atmosphere is argon atmosphere, and reduction is performed under a positive pressure of 1 atmospheric pressure or greater;

6. The manufacturing method of high purity hafnium according to any one of paragraphs 3 to 5 above, wherein electron beam melting is further performed to the hafnium sponge in order to obtain a hafnium ingot;

7. The manufacturing method of high purity hafnium according to any one of paragraphs 3 to 6 above, wherein hafnium chloride is reduced with metal having stronger chloridization power than hafnium;

8. The manufacturing method of high purity hafnium according to any one of paragraphs 3 to 7 above, wherein the zirconium content is 1 to 1000wtppm, and the purity thereof is 4N to 6N excluding gas components such as carbon, oxygen and nitrogen; and

9. The manufacturing method of high purity hafnium according to paragraph 8 above, wherein oxygen is 100wtppm or less, nitrogen and carbon are respectively 30wtppm or less, iron, chromium and nickel are respectively 5wtppm or less, and the purity thereof is 4N to 6N excluding gas components such as carbon, oxygen and nitrogen.

Effect of the Invention

The present invention yields a superior effect in that high purity hafnium can be stably manufactured by removing zirconium from the hafnium chloride aqueous solution via solvent extraction, reducing this to obtain a hafnium sponge, thereafter performing electron beam melting to this hafnium sponge, and thereby efficiently removing zirconium.

Further, the present invention yields an effect in that a high purity hafnium thin film can be obtained by manufacturing a sputtering target from the high purity hafnium ingot obtained with the foregoing process, and using this target to perform sputtering.

BEST MODE FOR CARRYING OUT THE INVENTION

In the present invention, the starting raw material will be zirconium tetrachloride ($HfCl_4$). A commercially available material can be used as the zirconium tetrachloride. This commercially available zirconium tetrachloride contains roughly 5wt% of zirconium.

This hafnium raw material, excluding zirconium, has a purity level of 3N, and contains, as main impurities other than zirconium, roughly 500wtppm, 40wtppm and 1000wtppm of iron, chromium and nickel, respectively.

First, this zirconium tetrachloride raw material is dissolved in purified water. Next, this is subject to multistage organic solvent extraction. Normally, solvent extraction is performed in 1 to 10 stages. TBP may be used as the organic solvent. As a result, zirconium can be made to be 1000wtppm or less, and normally 1 to 200wtppm.

Next, neutralization treatment is performed to obtain hafnium oxide (HfO_2). This hafnium oxide is subject to chlorination to obtain high purity zirconium tetrachloride ($HfCl_4$), and this is further reduced with, for instance, magnesium

metal having chloridization power that is stronger than hafnium or zirconium to obtain a hafnium sponge. As the reducing metal, in addition to magnesium, for instance, calcium, sodium, and so on may be used.

In order to efficiently perform the reduction treatment, it is desirable to make the moisture content in the hafnium chloride before reduction and in the atmosphere 0.1wt% or less, and the nitrogen content therein 0.1wt% or less. Further, when argon atmosphere is the reduction atmosphere, it is desirable to perform the reduction under a positive pressure of 1 atmospheric pressure or greater.

The obtained hafnium sponge may be further subject to electron beam melting for removing volatile elements, gas components and so on in order to increase the purity thereof.

According to the foregoing process, obtained is a high purity hafnium ingot wherein zirconium is 1 to 1000wtppm and having a purity of 4N (99.99wt%) or more excluding gas components such as carbon, oxygen and nitrogen; a high purity hafnium material wherein zirconium is 1 to 1000wtppm, oxygen is 100wtppm or less, nitrogen and carbon are respectively 30wtppm or less, iron, chrome and nickel are respectively 5wtppm or less, and having a purity of 4N to 6N excluding gas components such as carbon, oxygen and nitrogen; and a target formed from such high purity hafnium material; and, by using this target to perform sputtering, the high purity hafnium material can be deposited on a substrate.

The target may be manufactured with the ordinary processing steps of forging, rolling, cutting, finishing (polishing) and so on. There is no particular limitation in the manufacturing method thereof, and the method may be selected arbitrarily.

According to the present manufacturing method, as described above, the zirconium content in the hafnium can be reduced down to 1wtppm, and a total purity of 6N can be achieved.

Examples

The Examples are now explained. Incidentally, these Examples are merely illustrative, and the present invention shall in no way be limited thereby. In other words, the present invention shall only be limited by the scope of claim for a patent, and shall include the various modifications other than the Examples of this invention.

(Example 1)

The present invention used 100g of commercially available zirconium tetrachloride ($HfCl_4$) having a purity of 3N and containing roughly 5000wtppm of zirconium as the raw material, and this was dissolved in 1L of purified water to obtain a nitric acid solution. This raw material contained 500wtppm, 40wtppm and 1000wtppm of iron, chromium and nickel, respectively, as its main impurities.

Next, this hafnium raw material was subject to 4-stage organic solvent extraction using TBP organic solvent, and neutralization treatment was performed to obtain hafnium oxide (HfO_2).

Further, this hafnium oxide was subject to chlorination to obtain high purity zirconium tetrachloride ($HfCl_4$), and then subject to magnesium reduction to obtain a hafnium sponge. In order to efficiently perform the reduction treatment, the moisture content in the hafnium chloride before reduction and in the atmosphere was made to be 0.1wt% or less, and the nitrogen content therein was made to be 0.1wt% or less. Moreover, the atmosphere was made to be argon atmosphere, and reduction was performed under a positive pressure of 1.2 atmospheric pressure.

The obtained hafnium sponge was further subject to electron beam melting to remove volatile elements, gas components and so on. As a result of the foregoing process, it was possible to obtain a high purity hafnium ingot having a purity level of 4N5 (99.995wt%) wherein zirconium is 80wtppm; iron, chrome and nickel are respectively 1wtppm, 0.2wtppm and 2wtppm; and oxygen, nitrogen and carbon are respectively 20wtppm, 10wtppm and 20wtppm.

The sputtering target obtained from this ingot was able to maintain high purity, and it was possible to form a high purity hafnium thin film having uniform characteristics on a substrate by performing sputtering such sputtering target.

(Example 2)

The present invention used 100g of commercially available zirconium tetrachloride ($HfCl_4$) having a purity of 2N5 and containing roughly 3500wtppm of zirconium as the raw material, and this was dissolved in 1L of purified water. This raw material contained 500wtppm, 100wtppm and 300wtppm of iron, chromium and nickel, respectively, as its main impurities.

Next, this hafnium raw material was subject to 6-stage organic solvent extraction using TBP organic solvent, and neutralization treatment was performed

to obtain hafnium oxide (HfO_2). Further, this hafnium oxide was subject to chlorination to obtain high purity zirconium tetrachloride ($HfCl_4$), and then subject to calcium reduction to obtain hafnium sponge.

In order to efficiently perform the reduction treatment, the moisture content in the hafnium chloride before reduction and in the atmosphere was made to be 0.1wt% or less, and the nitrogen content therein was made to be 0.05wt% or less. Moreover, the atmosphere was made to be argon atmosphere, and reduction was performed under a positive pressure of 2 atmospheric pressure.

The obtained hafnium sponge was further subject to electron beam melting to remove volatile elements, gas components and so on. As a result of the foregoing process, it was possible to obtain a high purity hafnium ingot having a purity level of 4N (99.99wt%) wherein zirconium is 600wtppm; iron, chrome and nickel are respectively 10wtppm, 2wtppm and 5wtppm; and oxygen, nitrogen and carbon are respectively 100wtppm, 30wtppm and 30wtppm.

The sputtering target obtained from this ingot was able to maintain high purity, and it was possible to form a high purity hafnium thin film having uniform characteristics on a substrate by performing sputtering such sputtering target.

(Example 3)

The present invention used 100g of commercially available zirconium tetrachloride ($HfCl_4$) having a purity of 3N5 and containing roughly 1200wtppm of zirconium as the raw material, and this was dissolved in 1L of purified water. This raw material contained 500wtppm, 100wtppm and 300wtppm of iron, chromium and nickel, respectively, as its main impurities.

Next, this hafnium raw material was subject to 20-stage organic solvent extraction using TBP organic solvent, and neutralization treatment was performed to obtain hafnium oxide (HfO_2). Further, this hafnium oxide was subject to chlorination to obtain high purity zirconium tetrachloride ($HfCl_4$), and then subject to sodium reduction to obtain hafnium sponge.

In order to efficiently perform the reduction treatment, the moisture content in the hafnium chloride before reduction and in the atmosphere was made to be 0.001wt%, and the nitrogen content therein was made to be 0.0001wt%. Moreover, the atmosphere was made to be argon atmosphere, and reduction was performed under a positive pressure of 1.5 atmospheric pressure.

The obtained hafnium sponge was further subject to electron beam melting

to remove volatile elements, gas components and so on. As a result of the foregoing process, it was possible to obtain a high purity hafnium ingot having a purity level of 6N (99.9999wt%) wherein zirconium is 5wtppm; iron, chrome and nickel are respectively 0.2wtppm, 0.01wtppm and 0.1wtppm; and oxygen, nitrogen and carbon are respectively 10wtppm, <10wtppm and <10wtppm.

The sputtering target obtained from this ingot was able to maintain high purity, and it was possible to form a high purity hafnium thin film having uniform characteristics on a substrate by performing sputtering such sputtering target.

Industrial Applicability

By removing zirconium from hafnium chloride aqueous solution of the present invention via solvent extraction, obtaining hafnium sponge via reducing said hafnium chloride, and thereafter performing electron beam melting to this hafnium sponge, zirconium can be efficiently removed, and extremely pure hafnium can be stably manufactured. Thus, such high purity hafnium can be used as a heat-resistant or corrosion-resistant material, or an electronic material or optical material.